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THE MOLECULAR MECHANISM OF COLLOIDAL BEHAVIOR

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY RUSSELL STARKEY BRACEWELL

ENTITLED THE MOLECULAR MECHANISM OF COLLOIDAL BEHAVIOR

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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Recommendation concurred in*

Committee on Final Examination*

*Required for doctor's degree but not for master's

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I

INTRODUCTION

This work was taken up as a continuation of the investigation by Stearn[101], in this laboratory, on the swelling of protein colloids in acid solutions.

In this study fibrin will be subjected to similar treatment in alkaline solutions and in solutions of non electrolytes. Also by a correlation of the structure of the protein molecule with swelling and adsorption measurements, with different protein colloids in acid and alkaline solutions, we may understand the nature of the adsorption. It will be of value to know whether this adsorption by the protein colloid takes place at random on the walls of the pockets,or occurs at perfectly definite points on the molecule.

Adsorption and swelling of protein colloids in acid and alkaline solutions are always found to go hand in hand. By studying the behavior in different systems we may draw conclusions regarding the molecular mechanism of the swelling. We also should expect that any information as to the nature of the adsorption will be a means of interpreting this phenomena.

II

HISTORICAL

The first study, on a colloid chemical basis of the swelling of protein colloids in acid and alkaline solutions, and the reduction of the swelling by the addition of a neutral salt, was made by Fischer[102]. Experimentally, he has established the analogy between protein colloids and body tissue by studying their behavior in various systems.

Herzog and Adler[103], using powdered hide, measured adsorption in acid solutions. For strong acids they obtained data, which, if the adsorption is plotted against the concentration of the external acid solution, shows the adsorption to increase rapidly, reaching a maximum at the low concentration of 0.05 N. For increased concentrations, up to 0.1 N the adsorption is approximately a constant. With weak acids, as acetic, their data shows a straight line. However, as in the case of strong acids, they did not take measurements at concentrations greater than 0.1 N. They assume that complications due to hydrolysis at higher concentrations are liable to enter in.

The equilibrium between gelatin and dilute hydrochloric acid solutions by Proctor[104] shows results analogous to these of Herzog and Adler. Proctor has advanced a theory, to explain the mechanism of the swelling. He assumes that the protein acts as a di-acid base, and forms a double salt with hydrochloric acid, similar to aniline hydro-chloride. This salt, he says, is highly dissociated at low concentrations, which produces an osmotic phenomena thus accounting for the swelling. Stearn (Loc. Cit.) has shown the inadequacy of this theory to fully explain the swelling behavior.

Stearn (Loc. Cit.) in his work has verified in part the experimental data of Fischer (Loc. Cit.), and has shown by further investigation that gelatin and blood fibrin have similar adsorption and

swelling properties. With fibrin in strong acid solutions the swelling curves show a maximum at a low concentration, (about 0.05 N) and with increasing concentrations of the external acid the swelling is knocked down to a height approximating the swelling in pure water. The adsorption curves also show a rapid increase at low concentration, approaching nearly a constant value at about the same concentration as the maximum swelling. With further increase of the acid concentration, up to 1.0 N, the adsorption shows little change.

In the case of weak acids the swelling increases rapidly at low concentrations, and contrary to the strong acids, gradually increases with further increasing concentration of the acid. For adsorption the curves are approximately straight lines.

The effect of the addition of a neutral salt showed the same effect in knocking down the swelling as increasing the concentration of the strong acids. It was found, however, that increasing the concentration of the salt, in acid solutions of equal normality, increased the adsorption of the acid.

In certain neutral salt solutions, Oskra[105], working with blood charcoal found negative adsorption: that is, the water was adsorbed in excess of the salt, thus making the solution finally more concentrated. Stearn (Loc. Cit.) using sodium chloride solution observed the same phenomena with blood fibrin. However, no data was obtained to determine the amount of adsorbed water.

Considerable work has been done in studying the nature of adsorption of dyes and gases by charcoal. Glassuer and Suida[106] found that by extracting soot with benzene, a substance is obtained which takes up dyes from aqueous solution. Soots, sugar charcoal and wood charcoal contain oxygen and hydrogen and those which contain the

most oxygen are found to be the most active absorbents. Further observations showed that equal amounts of the same charcoal, under the same conditions will take up approximately the same amount of dye from a dilute or concentrated solution.

Knecht[107] has shown that the affinity of animal charcoal for crystal scarlet varies with the percentage of nitrogen in the charcoal. Also that the affinity for basic dyes, such as methylene blue may be decreased by heating the charcoal with zinc dust, and then treating successively with hydrochloric and hydroflouric acids. He points out in discussing other forms of charcoal such as cocoanut charcoal, lamp black,acetylene black, and naphthalene black, that the more closely the substance approaches pure carbon in composition the less is its decolorizing property.

Hunter[108], using charcoal as the absorbent, and using fairly high concentrations, has shown that with a solution of water and ammonia, the amount of the latter adsorbed may be varied by change of concentration. He explains this by saying that the two constituents of the solution are adsorbed separately. The pure water adsorbed then dissolves or adsorbs ammonia, the amount being a function of the concentration, thus increasing the amount of ammonia apparently adsorbed.

The structure of the protein molecule has been fairly definitely proven. The theory that the protein was made up of amino acids, the carboxyl group of one combined with the amino group of the other, was first suggested by Kossel and largely proven by the extensive work of E. Fischer.

Recent work on the free amino and carboxyl groups of the protein molecule are of particular interest. Van Slyke and Birchard[109],

with confirmation by Sure and Hart[110], have shown that the free amino nitrogen in several proteins investigated was approximately equal to one-half the lysine nitrogen. In other words the α-amino group adjacent to the carboxyl group is bound up in the peptid linkage, and the E-amino group is free. They state that the amino group on the guanidine end of the arginine molecule is probably in the free form, but that their methods of analysis are not suitable for determining nitrogen in this group.

Osborne, Leavenworth and Brautlecht[111] have proven that for most proteins the di-carboxyl acids are linked up in such a way that one of the carboxyl groups remains free. Exceptions to the rule are the proteins of the cereals. Gliaden as an example showed fewer free carboxyl groups than calculated from the percentages of glutamic and aspartic acids in the protein.

III

THEORETICAL

In view of the experimental results, Tolman and Stearn[112] have established a theory on the molecular mechanism of the swelling in protein colloids which seems highly probable. Briefly the theory follows: "In accordance with their amphoteric nature protein colloids have a marked tendency to adsorb hydrogen ions from acid solution and hydroxide ions from alkaline solutions. The adsorbed ions, together with a corresponding number of anions or cations as the case may be, form a double layer on the walls of the pockets or pores on the interior of the gel, and this leads to swelling and imbibition of water by electrostatic repulsion. The addition of a strong electrolyte to such a swollen colloid, either a neutral salt or an excess of the strong acid or alkali which caused the original swelling, will furnish ions in the interior of the pockets which will arrange themselves so as to neutralize the electrical field of the adsorbed layer, and thus bring about reduction in swelling. The addition of a neutral salt to an acid or alkaline solution tends to neutralize the electrical field of the adsorbed acid, and hence make it easier for more acid to get to the surface of the pockets, thus leading to increased adsorption."

If the above theory is correct we shall expect to find the behavior of fibrin in alkaline solution to run parallel to that in acid solution. In the one case the cation has been assumed to take the active part and in the second case the anion, yet in each the other ions arrange themselves in such a way as to perform their secondary though important function.

The above theory will hold whether we find the ions to be adsorbed at certain points on the protein molecule, or uniformly coated over the walls of the pockets. However, we should expect to throw

some light on the swelling phenomena by getting at the nature of the adsorption.

In discussing adsorption, Ashley[113] takes up the nature of this phenomena. In part he says: "It is generally thought that adsorption is a surface phenomena, and hence purely physical in character, which in many cases is doubtless true. But in other cases there is good evidence that a part is played by the purely chemical effects, which predominate to such an extent that the physical effects may be neglected entirely."

Although we do not wish to distinguish between chemical and physical adsorption as Ashley in part has done, yet we note that the discussion is an argument in favor of adsorption from a chemical standpoint.

Glassner and Suida (Loc. Cit.) and Knecht (Loc. Cit.) in view of their work with different forms of carbon believe that animal charcoal owes its decolorizing action to the presence of organic compounds stable at red heat; that absolutely pure carbon would be devoid of any decolorizing action. If there is any relation between the adsorption of acid and basic dyes by animal charcoal, and adsorption of acid and alkalies by protein colloids we should expect that a sample of charred fibrin would retain at least part of the adsorption properties of the original sample. This was verified by reducing a sample of fibrin in an open crucible at red heat to charcoal and measuring the adsorption in acid solution. An adsorption value equal to about twenty-five percent of the normal was obtained.

Since we know fairly definitely the structure of the protein molecule we might predict certain points that would have greatest attraction for the hydrogen ion, and other points that would have the

greatest affinity for the hydroxyl ion. With these assumptions, and knowing the percentage of the different amino acids in the protein, we may calculate the mols of acid or alkalie that would be adsorbed. The experimental data on adsorption offers a check on these calculations.

We might expect that when all such points had been satisfied, we could force the adsorption to take place at other points having less affinity.

It will be convenient to consider this chemical phenomena a special case in which the affinity of the ions is small compared to the usual type of chemical reaction. The fact that fibrin which has swollen and adsorbed acid in acid solution, may be freed from this acid by repeated washing in water leads us to the above theory. With this type of reaction the equilibrium of the unadsorbed and adsorbed ions will be a function of the ion concentration rather than the concentration of the acid.

IV

EXPERIMENTAL METHODS

As the present work was carried on as a continuation of the work of Stearn (Loc. Cit.) the experimental methods were followed out in much the same manner except where modifications were expedient.

THE MATERIALS- The blood fibrin was a sample of Merck's prepared as described by Stearn. A modification in washing the fibrin free from acid was found suitable. Instead of washing with distilled water and decanting, the mass of fibrin, contained in a towel was placed in a large funnel and water allowed to run down over the same in such a way that the mass was always covered with water.

The Gliaden and Casein were samples prepared by graduate students in the Laboratory of Physiological Chemistry. The acids and salts were the ordinary "C.P." reagents. The saccharose was the ordinary cane sugar of commerce. The raffinose used was a sample of Kahlbaums.

THE SWELLINGS,- These measurements were carried out exactly as described by Stearn.

THE ADSORPTION- The adsorption experiments were carried out in 250 cc. ground glass stoppered bottles. In the acid and alkali experiments the supernatent solutions were titrated against standard solutions. If on standing the protein went into solution the supernatent liquid was drawn off without shaking up the solution. The acid was standardized with sodium carbonate prepared from the bi-carbonate, and the alkali then standardized against the acid.

The number of mols of acid or alkali adsorbed per g. of fibrin was calculated by the following formula: $A = \frac{(Co - C)\ V}{W}$ where Co is the original concentration of the solution in mols per liter, C the reduced concentration after the adsorption has taken place, V the volume in liters of solution employed, and W the weight of fibrin

in grams.

The measurement of the negative adsorption in sugar solutions was carried out in a manner similar to the above. A small amount of phenol was added to the sugar solution to prevent decomposition. The concentrations were determined with a Lippich Large Universal Polariscope. The percentage sugar in solution was calculated by the well known formula $P = \frac{100 \times \alpha}{D \times (\alpha)^D_T \times l}$ where P is the percentage of sugar in the solution, α the observed angular rotation, D the density of the solution, $(\alpha)^D$ the specific rotation of the sugar under investigation and l the length of the tube in decimeters. A four decimeter tube was used in the analysis. The number of mols of water, A, adsorbed per gm. of fibrin was calculated by the following formula.

$$A = \frac{W(P_1 - P_2)}{p_1 \times W \times 18}$$

where W is the weight in grams of the solution taken, p_1 the final concentration of the sugar, p_2 the original concentration, W the weight of fibrin in grams.

For saccharose $(\alpha)^D$ was taken as 66.5 and for raffinose $(\alpha)^D$ was taken as 104.5. Since we were interested mainly in the change of concentration it was not necessary to correct for the value of $(\alpha)^D$ for different values of concentrations. For convenience a certain volume of sugar solution was used and the density determined by means of specific gravity bottle.

V

EXPERIMENTAL RESULTS

Adsorption of Acid and Swelling in Acid Solutions.

The behavior of fibrin in nitric and hydrochloric acids was first studied as a check on the previous work mentioned. The same type of curves were obtained although the adsorption measurements were some higher and the swelling observations a little less.

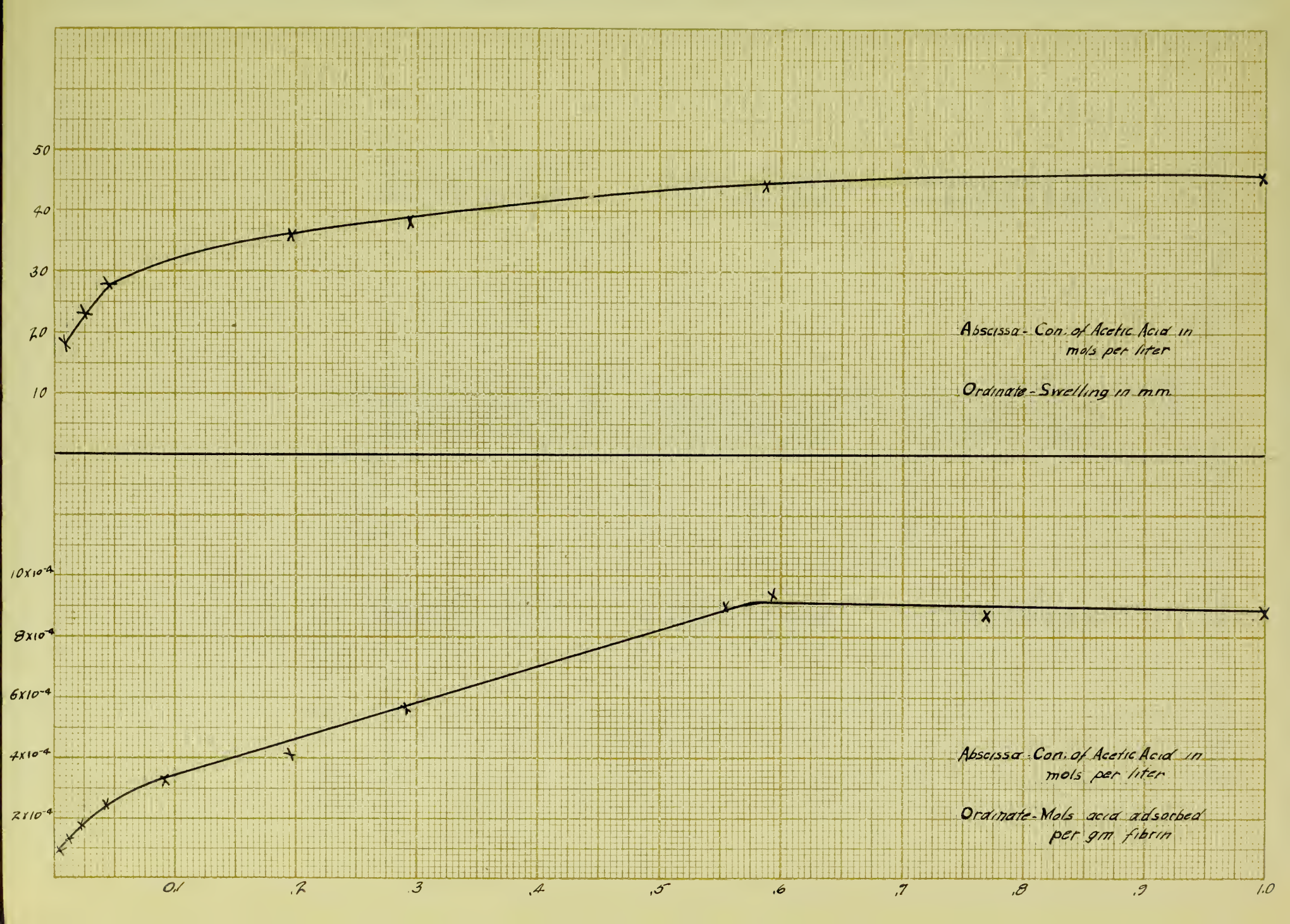
The following data was obtained with acetic acid.

C = Final concentration of external solution.

M = Mols adsorbed per gram of fibrin.

h = Height of swelling in millimeters.

C	M	h
.0082	.00009	-
.0173	.00013	19
.0263	.00018	24
.0462	.00025	29
.0954	.00033	30
.1970	.00042	37
.2936	.00057	39
.5950	.00095	45
.9980	.00090	45
		Water Control 9


50
40
30
20
10
Abscissa - Con. of Acetic Acid in mols per liter
Ordinate - Swelling in m.m.
10x10⁻⁴
8x10⁻⁴
6x10⁻⁴
4x10⁻⁴
2x10⁻⁴
Abscissa - Con. of Acetic Acid in mols per liter
Ordinate - Mols acid adsorbed per gm fibrin
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

Adsorption of Alkali and Swelling in Alkali Solutions

NaOH

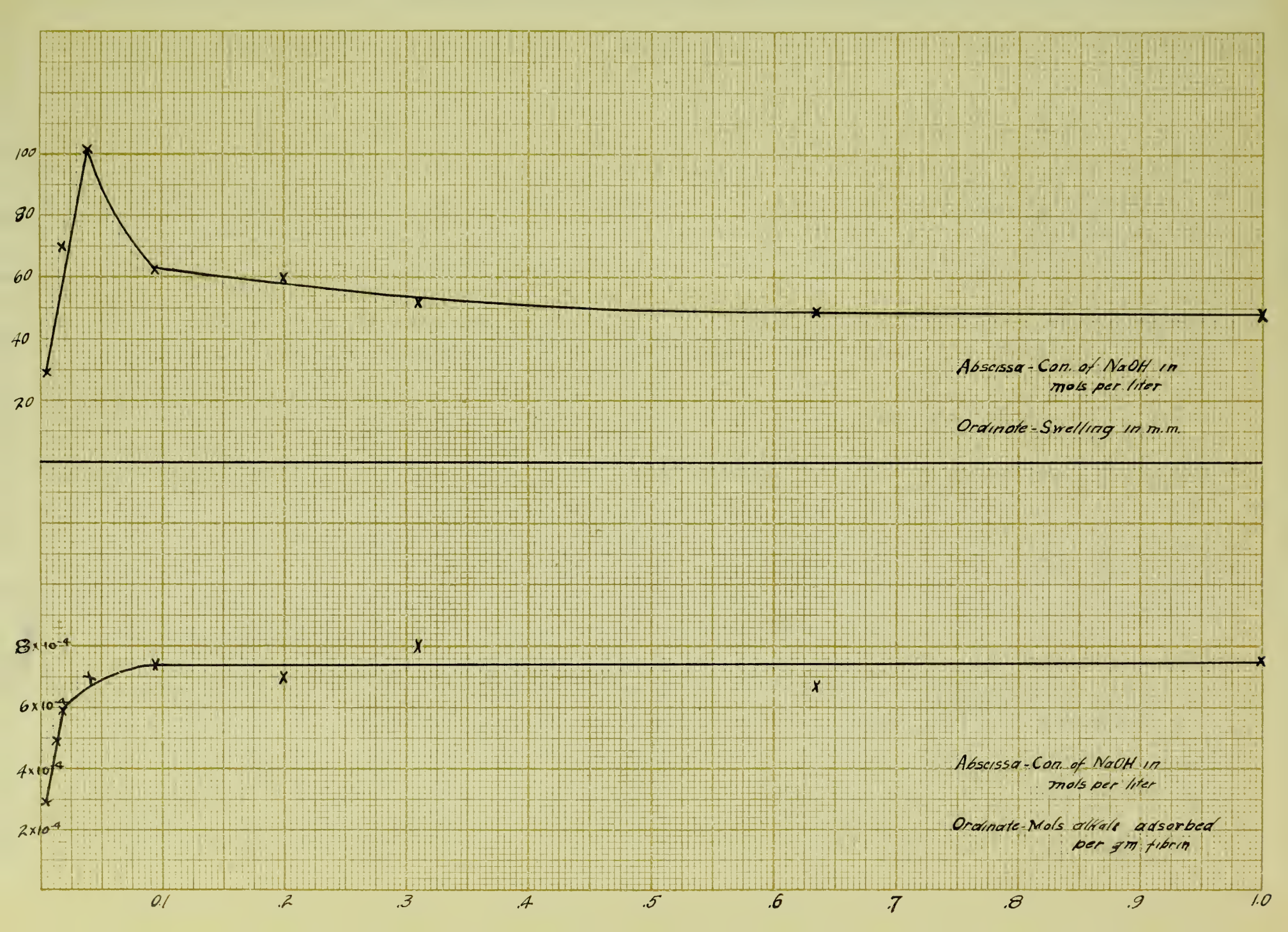
C	M	h
.0052	.00028	29
.0121	.00049	68
.0161	.00059	69
.0401	.00070	102
.0941	.00074	62
.1988	.00070	60
.3124	.00080	52
.6352	.00067	49
1.085	.00075	48
	Water Control	9

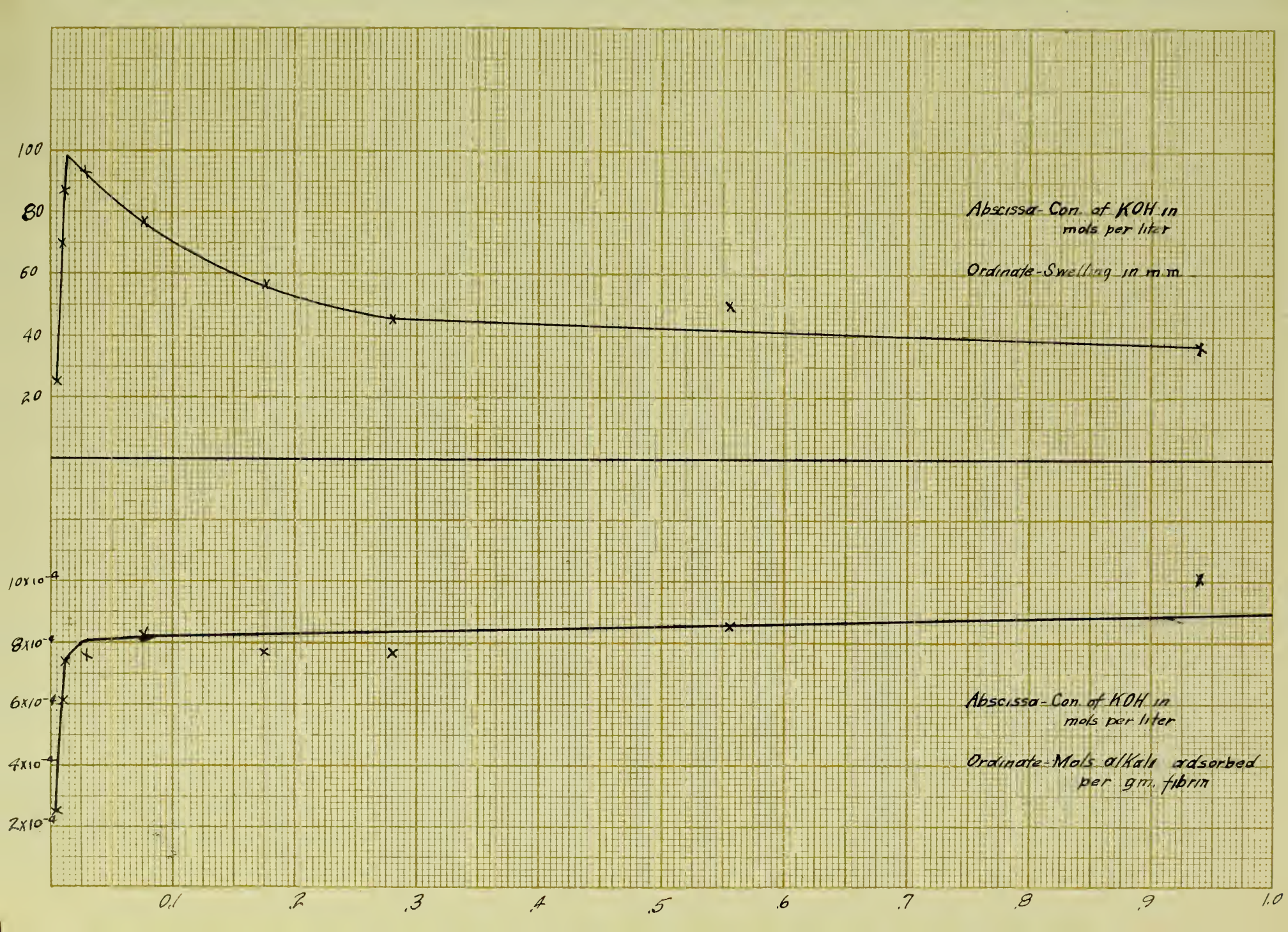
KOH

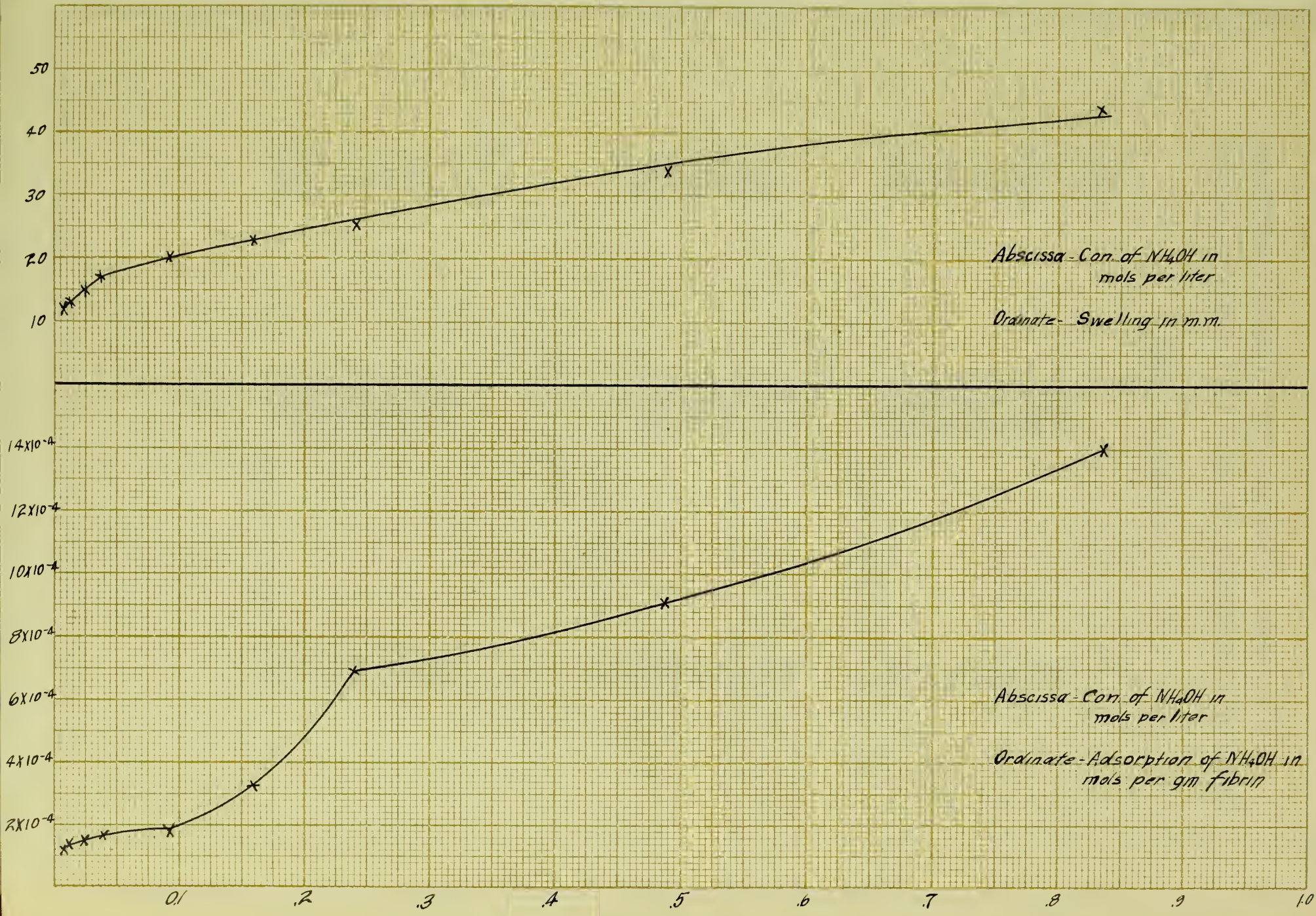
.0054	.00025	25
.0109	.00061	70
.0135	.00074	87
.0310	.00076	91
.0797	.00083	77
.1738	.00077	55
.2788	.00076	44
.5568	.00085	50
.9370	.00110	37
	Water Control	9

NH_4OH

.0072	.00012	12
.0154	.00014	13
.0241	.00015	15
.0403	.00017	17
.0833	.00018	20
.1613	.00033	23
.2388	.00069	25
.4855	.00091	34
.836	.00140	44
	Water Control	9


100
80
60
40
20
Abscissa - Con. of NaOH in mols per liter
Ordinate - Swelling in m.m.
8x10⁻⁴
6x10⁻⁴
4x10⁻⁴
2x10⁻⁴
Abscissa - Con. of NaOH in mols per liter
Ordinate - Mols alkali adsorbed per gm fibrin
0.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0


100
80
60
40
20
Abscissa - Con. of KOH in mols per liter
Ordinate - Swelling in m.m.
10x10-4
8x10-4
6x10-4
4x10-4
2x10-4
Abscissa - Con. of KOH in mols per liter
Ordinate - Mols alkali adsorbed per gm. fibrin
0.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0


50
40
30
20
10
Abscissa - Con. of NH4OH in mols per liter
Ordinate - Swelling in m.m.
14X10-4
12X10-4
10X10-4
8X10-4
6X10-4
4X10-4
2X10-4
Abscissa - Con. of NH4OH in mols per liter
Ordinate - Adsorption of NH4OH in mols per gm fibrin
0.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

Adsorption of alkali and swelling in equal concentration of alkali and varying concentration of salts.

NaOH (.0145 N)

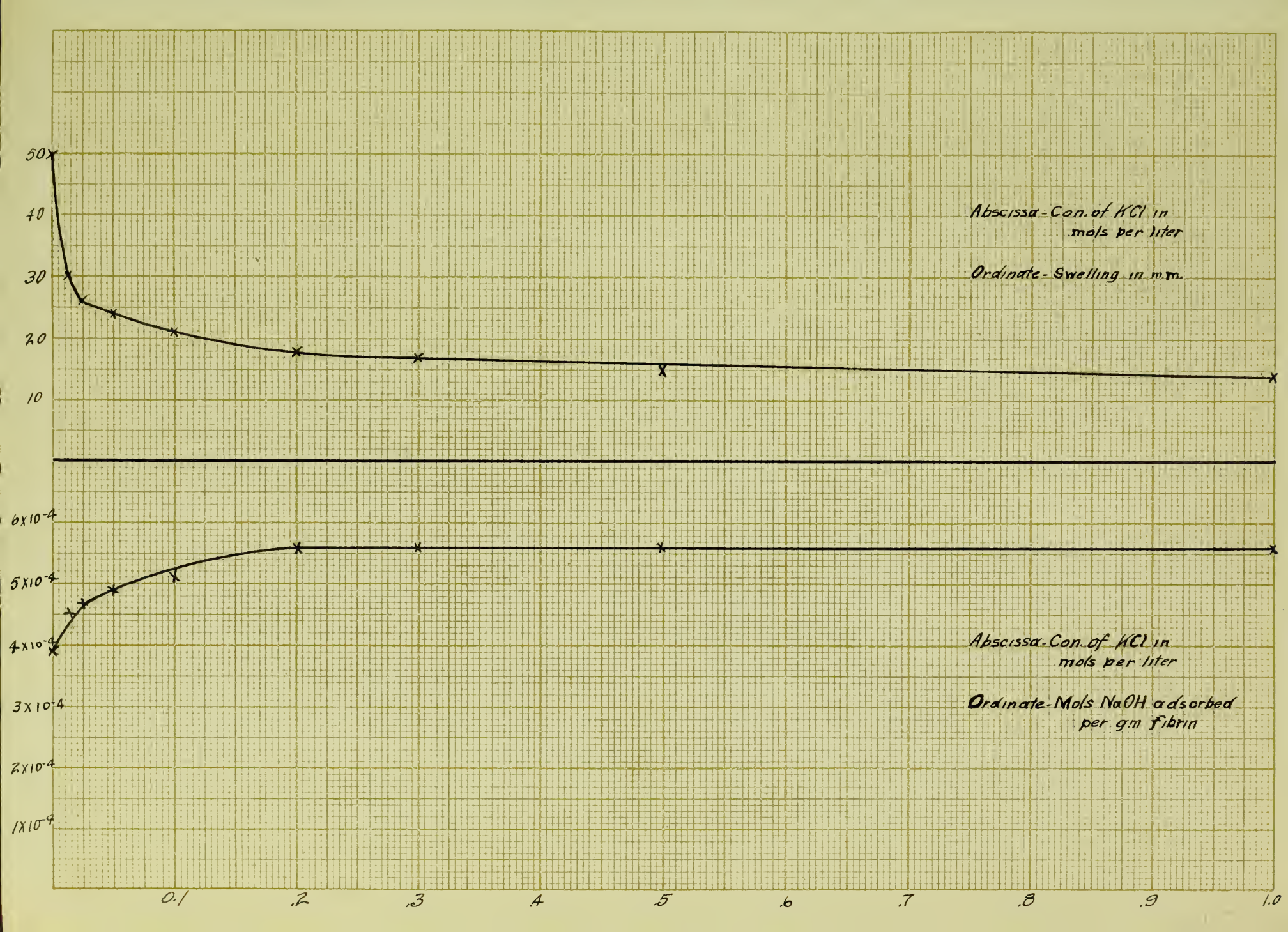
C_{KCl}	M	h
.0	.00039	50
.015	.00045	30
.025	.00046	26
.050	.00049	24
.100	.00051	21
.200	.00056	18
.300	.00056	17
.500	.00056	15
1.000	.00056	14
	Water Control	9

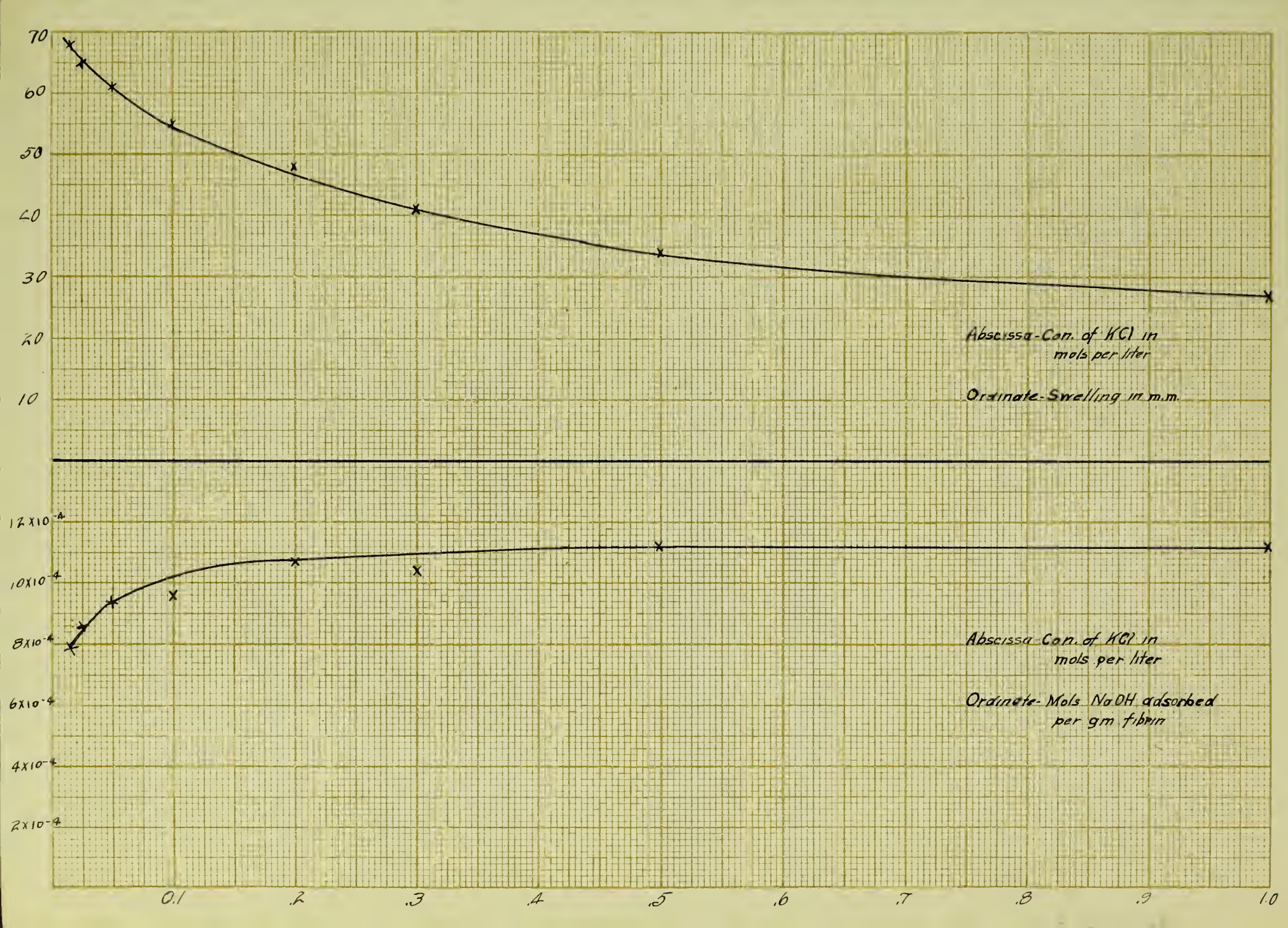
NaOH (.134 N)

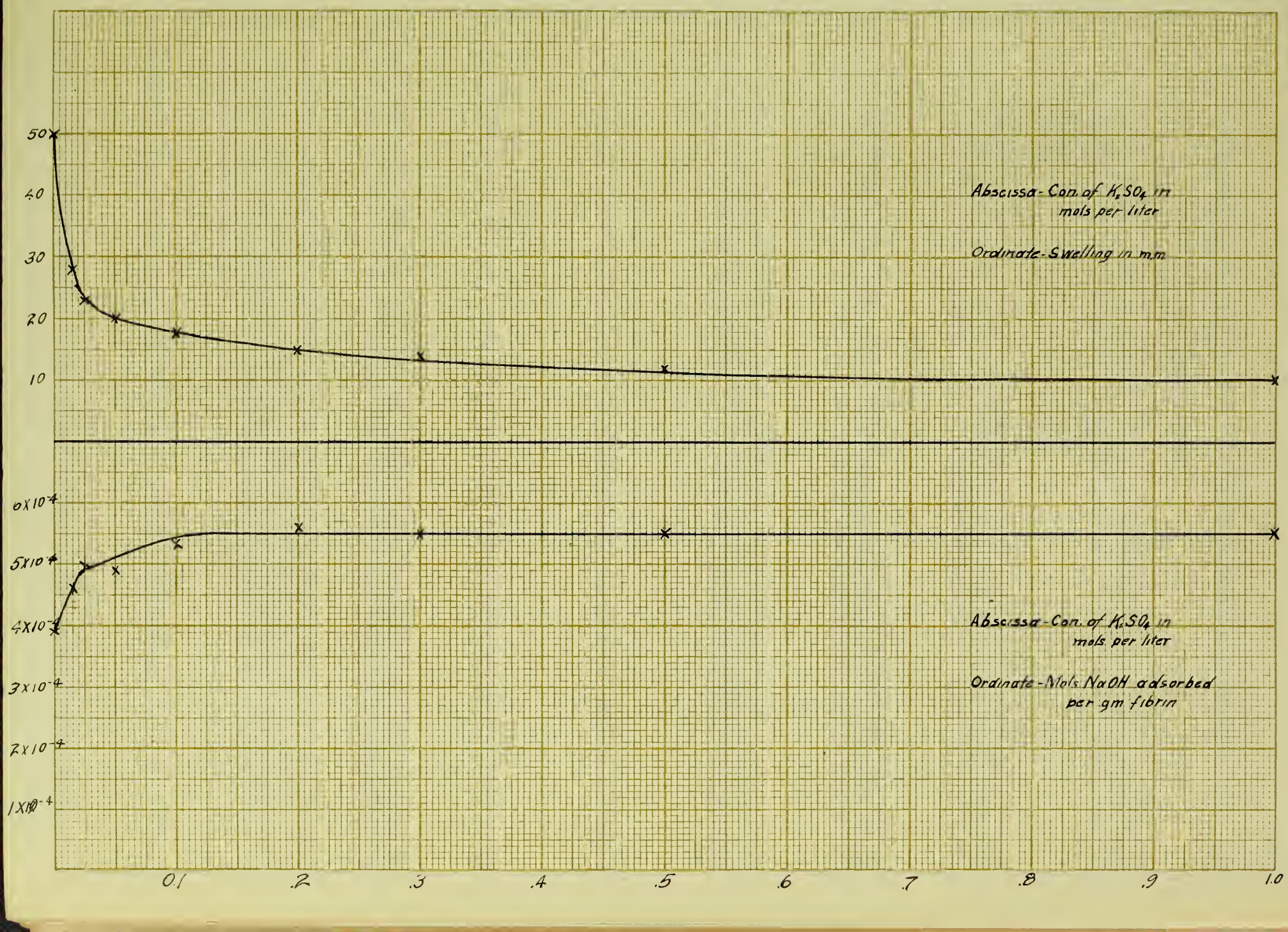
.0	.00072	68
.015	.00079	68
.025	.00086	65
.050	.00094	61
.100	.00095	55
.200	.00107	48
.300	.00104	41
.500	.00112	34
1.00	.00112	27
	Water Control	9

NaOH (.0144 N)

$C_{K_2SO_4}$	M	h
.0	.00039	50
.015	.00046	28
.025.	.00050	23
.050	.00049	20
.100	.00053	18
.200	.00056	15
.300	.00055	14
.500	.00055	12
1.000	.00055	10
	Water Control	9


50
40
30
20
10
Abscissa - Con. of KCl in mols per liter
Ordinate - Swelling in m.m.
6X10-4
5X10-4
4X10-4
3X10-4
2X10-4
1X10-4
Abscissa - Con. of KCl in mols per liter
Ordinate - Mols NaOH adsorbed per gm fibrin
0.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0


70
60
50
40
30
20
10
Abscissa-Con. of KCl in mols per liter
Ordinate-Swelling in m.m.
12X10-4
10X10-4
8X10-4
6X10-4
4X10-4
2X10-4
Abscissa Con. of KCl in mols per liter
Ordinate- Mols NaOH adsorbed per gm fibrin
0.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0


50
40
30
20
10
Abscissa - Con. of K_2SO_4 in mols per liter
Ordinate - Swelling in m.m.
$6X10^{-4}$
$5X10^{-4}$
$4X10^{-4}$
$3X10^{-4}$
$2X10^{-4}$
$1X10^{-4}$
Abscissa - Con. of K_2SO_4 in mols per liter
Ordinate - Mols NaOH adsorbed per gm fibrin
0.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

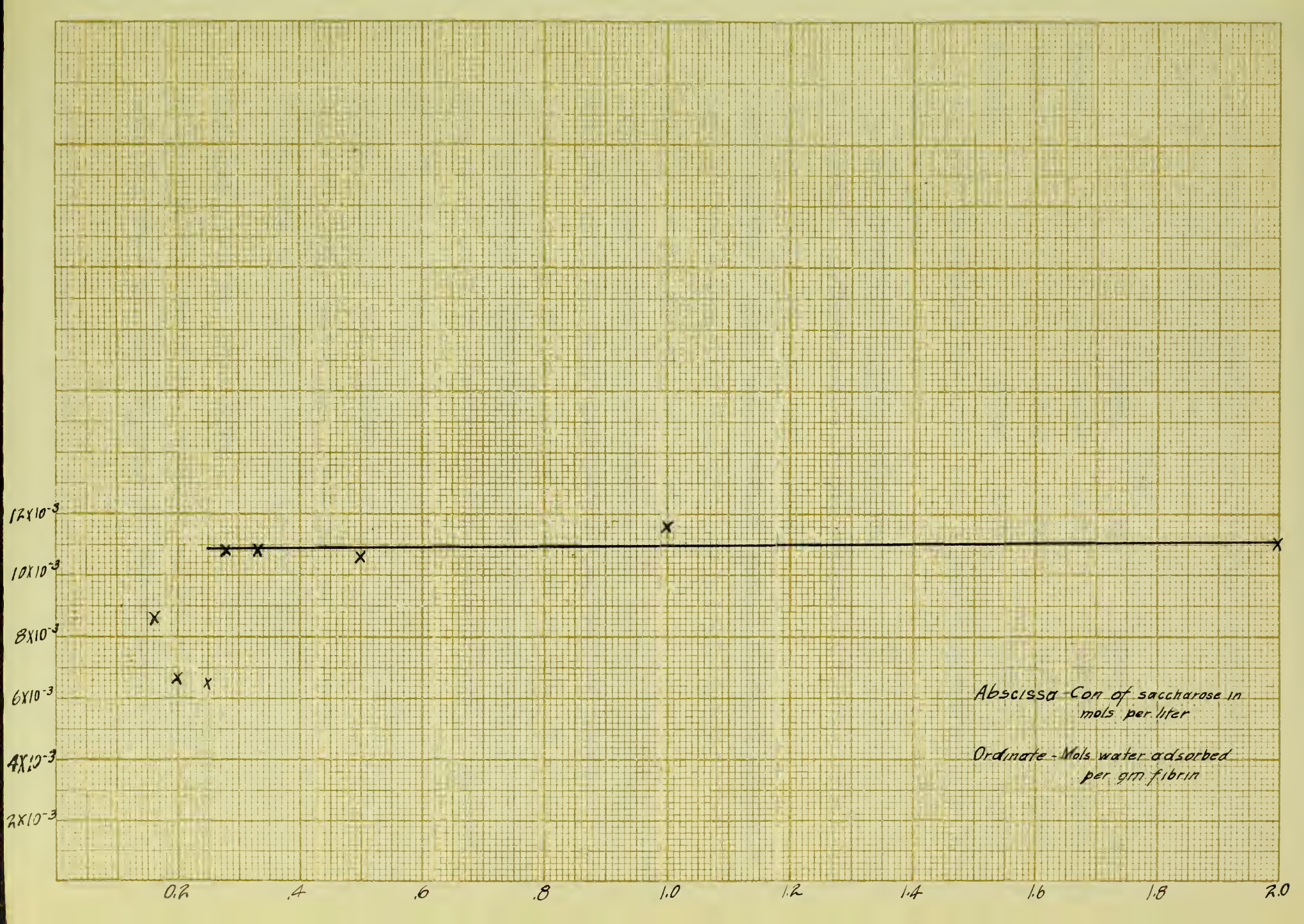
Adsorption of Water and Swelling in Sugar Solutions.

Saccharose

C	M		h
2.00	.0094		7
1.00	.0064		9
0.50	.0107		9
0.33	.0108		9
0.29	.0105		9
0.25	.0117		9
0.20	.0109		9
		Water Control	9

Raffinose

0.225	.0200		9
		Water Control	9


12X10⁻³
10X10⁻³
8X10⁻³
6X10⁻³
4X10⁻³
2X10⁻³
0.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
Abscissa - Con of saccharose in mols per liter
Ordinate - Mols water adsorbed per gm fibrin

Data comparing the adsorption of acid and alkali as calculated compared to that found experimentally.

	M_{acid}		M_{alkali}	
	calc.	ex.	calc.	ex.
Fibrin	.00109	.00096	.00082	.00078
Casein	.00063	.00053	.00125	.00120
Gliaden	.00020	.00028	.0030	.00110

In order to explain the above data a sample calculation for fibrin will be given.

Mol. wt. of fibrin - 14708 (Mathews)

1 ÷ 14708 = .0000679 mols in 1 gm. fibrin.

glutamic acid - mol. wt. 147 - 10.4%

14708 x 10.4% = 1529.6 gms. glutamic acid per mol. of fibrin.

1529.6 ÷ 147 = 10.4 mols glutamic acid per mol fibrin.

Aspartic Acid - mol wt. 133 - 10.4%

14708 x 2.0% = 294.16 gms. aspartic acid per mol. of fibrin.

294.16 ÷ 133 = 2.1 mols aspartic acid per mol. of fibrin.

10.4 + 2.1 = 12± mols di-carboxylic acids per mol. of fibrin.

12 x .0000697 = .00082 Mols di-carboxylic acids per gm. of fibrin

This value is to be compared with the mols of alkali adsorbed per gm. of fibrin.

Lysine - mol wt. 146 - 10.0%

14708 x 10.2% = 1470.8 gms. lysine per mol of fibrin

14708 ÷ 146 = 10 mols lysine per mol of fibrin

Arginine - mol wt. 174 - 6.9%

14708 x 6.9% = 1048.5 gms. arginine per mol of fibrin

1048.5 ÷ 174 = 6.0 mols arginine per mol of fibrin.

16 x .00068 = .000109 mols di-amino acids per gm. of fibrin

This value is to be compared to the mols of acid adsorbed per gm. of fibrin.

VI

DISCUSSION OF RESULTS

AND

CONCLUSIONS.

Discussion of Results.

The behavior of fibrin in strong alkalies as noted by the curves (Plates II and III) is very similar to the behavior in strong acids as found by Stearn. We may therefore consider this as additional confirmation of the general theory.

In checking up Stearn's data with the weak acids different types of adsorption curves were obtained. Instead of a straight line a curve of type similar to that of the strong acids was found, differing only in that it reached a maximum value at about 0.6 N instead of the low concentration of 0.02 N. Investigation showed that for adsorption measurements, in this case the evaporation of water from the finger bowls used by Stearn affected the data appreciably and made the curve appear as a straight line.

It is noted that the adsorption curve for acetic acid, over the concentrations used by Herzog and Adler[103] in measuring adsorption by powdered hide is approximately a straight line. If they had taken measurements at a higher concentration they very probably would have found a bend in the curve at a concentration near that given by the fibrin. They state that higher concentrations were not used because hydrolysis would enter in to complicate matters. The fact that in strong acids and alkalies and in weak acids the adsorption reaches a constant value and continues approximately so up to 1.0 N shows that no hydrolysis has taken place.

From the straight line obtained representing the adsorption of acetic acid, Stearn reasoned that the adsorption would increase to higher concentrations. He notes that at 10.0 N the adsorption of acid had increased about tenfold. It is difficult to measure such values at a high concentration, but measurements with hydrochloric

acid at this high normality gave results which were hardly more than qualitative, yet indicated values similar to Stearns. We should expect that at such high concentrations a more or less breaking up of the protein by strong reagents and hence not a true indication of the adsorption.

The above results do not mean a non-conformity to the theory yet it will eliminate the explanation that with increased swelling the pockets are opened up to furnish new surfaces where adsorption will take place.

The data for the ammonium hydroxide is a little difficult for interpretation. The points on the graph representing the adsorption show two distinct types of curves. For low concentrations the curve is similar to the others found in adsorption work, but for higher concentrations the curve is concave upwards, which suggests that some other type of adsorption, or some factor other than adsorption is coming in. Comparing the experimental value at 0.9 N concentration with that calculated from the theoretical consideration we find nearly twice the amount adsorbed that we should expect. This is further evidence of the above conclusions. We may interpret the behavior of fibrin in ammonium hydroxide on the basis of an analogy similar to observation of Hunter (Loc. Cit.) with charcoal and this alkalie. It will be necessary to assume that the alkali apparently adsorbed is effective in producing swelling as well as that of the true adsorption or that increasing the concentration decreases the dielectric properties of the solution, since the swelling curve does not show a maximum value.

The effect of the addition of neutral salts to swollen protein colloids in alkaline solution is similar to the results obtained by

Stearn in acid solutions. It is noted that in equi- molar concentrations of potassium chloride and potassium sulfate the divalent salt is most effective in decreasing the swelling. However, the former apparently was just as effective in increasing the adsorption.

Using a low concentration of alkali which corresponded to less than the maximum adsorption by fibrin the addition of the neutral salt is shown to increase the adsorption to a constant value, a little less than the maximum in higher concentrations of alkali. By using a concentration of alkali which corresponded to a maximum adsorption it is noted that the adsorption is again increased. We may conclude that the presence of the neutral salt has the power of inducing adsorption of the hydroxide ions at secondary points on the protein molecule which have less affinity.

With the sugar solution we have verified the adsorption of water by fibrin. We should expect that with the acid and alkaline solutions water will also be adsorbed and that the measurements in these solutions will not be a true measure of the adsorption. However, if we assume an amount of water adsorbed equal to that adsorbed from the sugar solution a short calculation shows that no appreciable error is introduced in neglecting this factor.

As there is no appreciable swelling accompanying the adsorption of water we will necessarily have to consider this type of adsorption different from the acid and alkali in which the ions are the main factor. It is probable that the water is adsorbed as a molecular film on the surface of the fibrin.

The adsorption of water is approximately a constant for varying concentrations of saccharose, but with raffinose shows a value about twice as great. Stearn's work with sodium chloride solution showed

about one-tenth as much water adsorbed as shown by saccharose. We must at least conclude that the amount of water adsorbed from solutions depends upon the nature of the solute.

The data in the nature of adsorption shows that for fibrin and casein the mols of acid or alkali adsorbed correspond closely to the amount predicted for each by taking the evidence that each di-amino acid molecule has one amino group, and each di-carboxyl acid molecule has one carboxyl group uncombined in the protein molecule. With the Gliaden the experimental and calculated values for acid adsorption check very well, but for the alkali adsorption do not. However, we should expect a low experimental value in view of the studies of Osborne, Leavonworth, and Brantlecht (Loc. Cit.) already mentioned.

It appears that the charge on the protein molecule holds the adsorbed ions loosely bound. This is in accord with the fact that by repeated washing with water, adsorbed acid or alkali may be removed. The charge on the adsorbed ions is in excess of the charge on the protein and hence produces the electrostatic effects. We may therefore, consider the adsorption of acid and alkalies by protein colloids as a loosely bound chemical effect.

Conclusions.

1. The behavior of fibrin in strong alkaline solution and the effect of the addition of a neutral salt is very similar to the behavior in strong acid solutions.

2. Adsorption in weak acids reaches a maximum value equal to that in strong acid solutions.

3. The swelling of fibrin in a solution of a weak base, as ammonium hydroxide, corresponds to the swelling in weak acid solutions. The abnormal adsorption is due to the peculiar adsorption properties of this solution of gas in water. (A normal weak base if available would probably show an adsorption curve very similar to that of weak acids.)

4. From solutions of some non electrolytes protein colloids adsorb water, at least the water is adsorbed in excess of the solute. This adsorption is a molecular phenomena.

5. In protein colloids hydrogen ions are adsorbed at points on the protein molecule where there are free amino groups and hydroxyl ions are adsorbed at points where there are free carboxyl groups.

6. The addition of a neutral salt induces adsorption of hydrogen ions and hydroxyl ions at other points having less affinity.

7. The adsorption of hydrogen and hydroxyl ions by protein colloids is a type of chemical reaction in which the affinity is small compared to the most general type of chemical reaction.

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VII

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